

PATENT SPECIFICATION

DRAWINGS ATTACHED

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935.013



935.013

Date of filing Complete Specification May 27, 1960.

Application Date May 27, 1959.

No. 18080/59.

Complete Specification Published Aug. 21, 1963.

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Index at acceptance: —Class 2(6), G(1BX:1C3:2C), G3A(1:3:4:5), G3(B:C2:), G4A.

International Classification:—C08f.

COMPLETE SPECIFICATION

Process for Manufacturing Graft Copolymers of Polyolefines and Styrene

We, B.X. PLASTICS LIMITED, a British Company, of Brantham Works, near Manningtree, Essex, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention provides a process for manufacturing a graft copolymer derived from a polyolefine and styrene, wherein a polyolefine film is contacted with styrene in the presence of an aliphatic polyamine at a temperature at which the styrene will swell the film to a significant extent but will not cause any substantial dissolution of the polyolefine film. As the polyolefine there comes into consideration, more especially, polyethylene.

Advantageously the contacting of the polyethylene film with styrene is carried out in the presence of an aliphatic polyamine, for example, a polyalkylene amine. As examples of aliphatic amines there may be mentioned dipropylene tetramine, 1:3-propylene diamine and especially tetraethylene pentamine.

The aliphatic polyamine may be added to the styrene, and the concentration of the aliphatic polyamine may be 0.01—1.0% calculated on the weight of the styrene.

Advantageously, the polyolefine film is treated so as to form polymerisation-initiating centres on it before being contacted with styrene.

The film may be pre-treated by subjecting it to thermal, ultra-violet or high energy ionising radiation prior to its contact with styrene. The polyethylene film may be subjected, for example, to electron irradiation.

When ultra-violet radiation having an energy level, for example, of about 5 e.v., is

used the grafting rate of the polyethylene film and styrene may be increased by incorporating a sensitizer, for example, benzophenone, into the polyethylene film prior to the irradiation.

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Advantageously the polyethylene film may be aged in air prior to contacting it with styrene.

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The polyethylene film may be composed of polyethylene having a low density and a relatively low crystallinity compared with low pressure polyethylene. The contacting of the low density polyethylene with styrene may be carried out at a temperature in the range of 40—70° C., advantageously 55—65° C. and more especially a temperature of substantially 60° C.

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Alternatively polyethylene of medium density may be used, in which the contacting of polyethylene with the styrene may be carried out at a temperature of from 40 to 90° C., for example 55 to 70° C.

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The polyethylene film may be composed of low pressure polyethylene, that is polyethylene having a high density and a high crystallinity. The contacting of the low pressure polyethylene with styrene may be carried out at a temperature in the range of 40—110° C., for example, 55 to 75° C.

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An improved grafting rate is obtained when the contact between the polyethylene film and styrene is carried out in the presence of an inert gas, for example, nitrogen. The nitrogen need not be entirely oxygen free. However, the grafting may be performed in a reaction-vessel open to air, but to prevent loss of styrene it is preferable to arrange the opening in the form of a narrow entry slit.

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A reproducible grafting rate is obtained when the contact between the polyethylene

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film and styrene is carried out in a reaction vessel constructed of stainless steel. Variations arise with other metals; for example, an accelerated grafting rate occurs with clean copper surfaces, while retarded grafting is observed with oxidised surfaces of copper or its alloys.

The process of the present invention is especially applicable to the continuous production of uniformly grafted films of polyethylene and styrene.

Such a process is exemplified in Example 1 below.

The graft copolymer of polyethylene and styrene obtained by the process of the present invention are especially suitable for conversion into perm-selective membranes by, for example, sulphonation to produce anionic sulphonic acid groups or chloromethylation followed by quaternisation to produce cationic quaternary ammonium groups.

Perm-selective membranes may be employed for purifying brackish water and sea water by the process of electrolytic deionisation, the principle of which depends on the selectivity of membranes separating electrode compartments, such that the membrane allows the passage of either positively charged ions or negatively charged ions but not both.

The utility and economy of electrolytic deionisation are limited by deficiencies of the perm-selective membranes such as (a) lack of chemical resistance, (b) low exchange efficiency, (c) high electrical resistance or (d) low mechanical strength.

The perm-selective membranes derived from the graft copolymers of polyethylene and styrene, obtained by the process of the present invention, are produced uniformly and inexpensively and are free from the above defects to a substantial extent, that is to say the membranes produced are strong, chemically inert and have a high exchange capacity and a high electrical conductivity in the swollen state.

Example 1 illustrates a continuous method of grafting styrene on to polyethylene film. Examples 2-9 illustrate the invention. "Teflon", "Bakelite", "Hanovia", "Alkathene", and "Propathene" are Registered Trade Marks.

EXAMPLE 1

The drawing accompanying the provisional specification illustrates diagrammatically a continuous method of manufacturing a graft of styrene on to polyethylene film.

Polyethylene film, fed from a roll (1) was irradiated by a suitable source (2) prior to entering a heated reaction vessel (3) containing a dilute solution of tetraethylene pentamine in distilled styrene monomer.

The reaction vessel was fitted with rollers (4) which form a festoon enabling a large area of film to remain in contact with monomer.

Atmospheric oxygen was excluded from the vessel by passing in a stream of nitrogen at (5) which was dispersed evenly through the monomer by a sintered stainless steel plate (6). Further protection against oxygen access was afforded by the narrow entry and exit grooves (7) and by the Teflon gasket (8) where the lid was secured to the vessel.

Replenishment of reactants and removal of homopolymer were effected by means of the tubes (9) and (10) respectively.

Excess monomer adhering to the grafted film was removed by passing the film through a drying chamber (II). The finished product was then collected on a roll (12).

EXAMPLE 2

A film of intermediate density polyethylene composed of Bakelite DFD 0111 containing 0.43% by weight of benzophenone was extruded as a layflat tube having a thickness of 0.005" and was irradiated under a Hanovia Ultra Violet lamp (UVS 3000). The polyethylene film was passed perpendicular to and at a distance of 6" from the arc tube, which was fitted with an AC reflector. The path length of the film through the irradiation zone was 12" and the film travelled at the speed of 7.5 to 8" per minute. The film was then cooled with an air blast.

0.1 gram of the pre-treated polyethylene film was then grafted under at atmosphere of nitrogen for 2 hours at 60° C. with 6 ml. of pure styrene monomer, that was dirt- and inhibitor-free and contained 0.2% by weight of commercial grade tetraethylene pentamine.

The weight increase of the dried film after removal from the styrene monomer was 21.6%. Some of the styrene monomer (0.4%) polymerised to styrene homopolymer.

EXAMPLE 3

0.1 gram of a low density polyethylene film composed of I.C.I. Alkathene Grade 7 and having a thickness of 0.005" was irradiated in air at room temperature by 2 Mev electrons from a Van de Graaf accelerator to a dose of 15 Megarads at a rate of 1 Megarad per pass at 10 minute intervals.

The polyethylene film was then grafted *in vacuo* for 6 hours at 60° C. with 6 ml of pure styrene monomer, that was dirt- and inhibitor-free and contained 0.2% by weight of commercial grade tetraethylene pentamine.

The weight increase of the dried film after removal from the styrene monomer was 76%. Some of the styrene monomer (1.12%) polymerised to styrene homopolymer.

A comparative experiment was carried out under the same conditions as described above using the styrene monomer free from tetraethylene pentamine. The weight increase of the polyethylene film was 15%, and 1.39% of the styrene monomer polymerised to styrene homopolymer.

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EXAMPLE 4

5 0.1 gram of a commercial low density polyethylene film composed of ICI Alkathene Grade 7 and having a thickness of 0.005 inch was heated while immersed in a purified styrene containing 0.2 per cent by weight of commercial-grade tetraethylene pentamine in a nitrogen atmosphere for 16 hours at 60° C. The weight increase of the dried film after removal from the styrene was 16.1 per cent. During the grafting, 1.4 per cent of the styrene was converted to homopolymer.

EXAMPLE 5

15 A sample of commercial, non-surface treated, freshly-extruded low density polythene film composed of ICI Alkathene Grade 7 was immersed in a 0.2% solution in styrene of tetraethylene pentamine for 19 hours at 60° C. in a nitrogen atmosphere.

40	Amine	Polystyrene Content of Grafted Film
	Amino ethyl ethanolamine	14.1
	Dipropylene tetramine	15.7
	1:3 propylene diamine	14.4
	Tetraethylene pentamine	17.4

45 Thus all the amines accelerated grafting of styrene to polythene but tetraethylene pentamine was the most effective for a given concentration.

EXAMPLE 7

50 A film of high-density polythene of thickness 0.005" and containing 0.2% by weight of benzophenone was irradiated under a Hanovia U.V. lamp (U.V. S, 3000) under the conditions of Example 2. Thereafter, the film was passed through the apparatus described in Example 1 and illustrated in Figure 1. The concentration of tetraethylene pentamine in styrene was maintained in the grafting cell at 0.2% by metered feed of distilled styrene and tetraethylene pentamine, and the film was fed through the cell at 65° C. at the rate of 1.25 inches per hour (corresponding to a contact time of 9.2 hours). The film was wound up on emergence and was subsequently analysed spectroscopically for polystyrene content at 6" intervals. The result of the analysis are shown in the table.

65	Distance	% Polystyrene in graft
70	6"	24.1
	12"	25.0
	18"	20.8
	24"	22.5
	30"	21.65
	36"	22.25

75 This table shows the uniformity of grafting achievable by the operation of this process.

EXAMPLE 8

(a) A 0.005" thick film of polypropylene (ICI Ltd. "Propathene") was Soxhlet-extracted in acetone, dried and then subjected,

The weight increase of the dried film after removal from the styrene was 8.4%. Spectroscopic analysis revealed the presence of 6.1% combined polystyrene. The same film held in pure styrene for the same length of time gave zero weight increase.

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EXAMPLE 6
To investigate the comparative activity of other aliphatic amines, samples of 0.005" high density polythene film, which had been previously activated with ultra-violet radiation under the conditions of Example 2 were immersed in 0.2% solutions in styrene of the amines listed below. The polystyrene contents of the dried films were determined after a 2 hour reaction time at 60° C. in a nitrogen atmosphere, and the results are given in the table.

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**Polystyrene Content
of Grafted Film**

-	14.1
-	15.7
-	14.4
-	17.4

in air, to irradiation by a Co-60 source until it had received a dose of one megarad. (This dose was estimated from the oxidation of ferrous ammonium sulphate placed in the irradiation field of the Co-60).

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(b) Portions of the film from 8(a) were immersed in freshly distilled styrene in glass tubes. After degassing under vacuum, the tubes were sealed. The tubes were then stored in a bath at 60° C. for periods ranging from 1 to 22 hours. After cooling, the films were taken from the tubes, wiped, dried under vacuum at 80° C., and then finally cooled and weighed. The changes of weight were:

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Time Film in Styrene at 60° C.	Percentage Increase in Hours	of Film Weight
1	3	95
5	10	
16½	46	
22	64	

All the films were translucent and tough; those with the higher styrene contents had become appreciably more rigid.

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(c) Portions of the film from 8(a) were submitted to the same processes as in 8(b), except that they were immersed at 60° C. in styrene containing 0.2% (by weight) of tetraethylene pentamine. The following table gives the changes of weight:

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Time Film in Styrene at 60° C.	Percentage Increase in Hours	of Film Weight
1	2	
2.8	9	
5.3	18	
7.3	21	

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All these films were translucent and tough and similar to those of 8(b).

Comparison of 8(b) and 8(c) shows the rate of grafting of styrene on polypropylene was increased when tetraethylene pentamine was present in the styrene in which the films had been immersed.

EXAMPLE 9

(a) A 0.002" thick film of polypropylene

20	Sample	Time Film in Styrene at 60°		C. Percentage Increase of Film Weight
		in Hours		
	A	1		0.5
	B	8		14.5
	C	15		34
	D	21 $\frac{1}{4}$		44

25 All these films were translucent and tough; those with the higher styrene contents had become appreciably more rigid.

(ICI Ltd. "Propathene") was irradiated, in air, by a Co-60 source to a dose of one megarad. The film was then Soxhlet-extracted in methylene chloride for 6 hours and then dried under vacuum at 40° C. for 4 hours.

10 (b) Portions of the film from 9(a) were then subjected to the processes of Example 8(b). The changes of weight were:—

30	Sample	Time Film in Styrene at 60°		C. Percentage Increase of Film Weight
		in Hours		
	V	2 $\frac{1}{4}$		8.8
	W	8		42.5
	X	15		76
	Z	21 $\frac{1}{4}$		74

40 All these films were translucent and tough; those with the higher styrene contents had become appreciably more rigid.

45 (d) The films of 9(b) and 9(c) were then kept immersed in toluene at 60° C. for 20 hours. They were then dried under vacuum at 80° C. to constant weight. After cooling they were weighed. Assuming grafted styrene would not be extracted by the toluene, the following table gives the percentage (by weight) of styrene grafted on the polypropylene.

50	Sample	% Grafted Styrene		C. Percentage Increase of Film Weight
	A	0		
	B	8		
	C	20		
	D	27		
55	V	6		
	W	36		
	X	66		
	Z	64		

60 These figures show clearly that a much higher proportion of the polymerized styrene was grafted on the polypropylene when tetraethylene pentamine was present in the styrene used in the grafting process.

65 **WHAT WE CLAIM IS:—**

1. A process for the manufacture of a graft copolymer derived from a polyolefine and styrene, wherein a polyolefine film is contacted with styrene in the presence of an aliphatic polyamine at a temperature at which the styrene will swell the film to a significant extent, but will not cause any substantial dissolution of the polyolefine film.

10 (ICI Ltd. "Propathene") was irradiated, in air, by a Co-60 source to a dose of one megarad. The film was then Soxhlet-extracted in methylene chloride for 6 hours and then dried under vacuum at 40° C. for 4 hours.

15 (b) Portions of the film from 9(a) were then subjected to the processes of Example 8(b). The changes of weight were:—

25 (c) Portions of the film from 9(a) were then subjected to the processes of Example 8(c).

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2. A process as claimed in Claim 1, wherein the polyolefine film is treated so as to form polymerization-initiating centres thereon, before being contacted with styrene.

3. A process as claimed in Claim 1 or 2, wherein the aliphatic polyamine is a polyalkylene amine.

4. A process as claimed in Claim 3, wherein the polyalkylene amine is tetraethylene pentamine.

5. A process as claimed in any one of Claims 1 to 4, wherein the aliphatic polyamine is used in a concentration of from 0.01 to 1.0 per cent calculated on the weight of the styrene.

6. A process as claimed in any one of Claims 1 to 5, wherein the polyolefine film is pre-treated by subjecting it to thermal, ultra-violet or high energy ionising radiation.

7. A process as claimed in Claim 6, wherein the polyolefin film is subjected to electron irradiation.

8. A process as claimed in Claim 6, wherein the polyolefine film is subjected to ultra-violet radiation in the presence of an ultra-violet sensitisier, for example, benzophenone.

9. A process as claimed in any one of Claims 1 to 8, wherein the polyolefine is polyethylene.

10. A process as claimed in Claim 9, wherein the polyethylene is of low density and the film is contacted with styrene at a temperature in the range 40 to 70° C.

11. A process as claimed in Claim 9, wherein the polyethylene is of medium den-

sity and the film is contacted with styrene at a temperature in the range of 40 to 90° C. 25

12. A process as claimed in Claim 9, wherein low pressure high density polyethylene is used and the film is contacted with styrene at a temperature in the range of 40 to 110° C. 5

13. A process as claimed in any one of Claims 1 to 8, wherein the polyolefine is polypropylene. 10

14. A process as claimed in any one of Claims 1 to 13, wherein the polyolefine film is contacted with styrene in an atmosphere that is substantially free from oxygen. 15

15. A process as claimed in Claim 14, wherein the polyolefine is contacted with styrene in an atmosphere of nitrogen. 20

16. A process as claimed in any one of Claims 1 to 15, wherein the contact between the polyolefine film and styrene is carried out in a reaction vessel constructed of stainless steel. 25

17. A process as claimed in any one of Claims 1 to 16, wherein the polyolefine film is aged in air prior to contacting it with styrene. 30

18. A process as claimed in any one of Claims 1 to 17, which is carried out in a continuous manner. 35

19. A process as claimed in Claim 1 which is carried out substantially as described in Example 1. 40

20. A process according to Claim 1 conducted substantially as described in any one of Examples 2—9 herein. 45

21. Graft copolymers of polyolefine and styrene, whenever made by the process claimed in any one of Claims 1 to 20.

22. Perm-selective membranes obtained from the graft copolymers claimed in Claim 20 by sulphonation to produce anionic sulphonate acid groups, or by chloromethylation followed by quaternisation to produce cationic quaternary ammonium groups on the graft copolymer.

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Quality House, Quality Court,
Chancery Lane, London, W.C.2.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

935013 PROVISIONAL SPECIFICATION
1 SHEET

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the Original on a reduced scale*

